

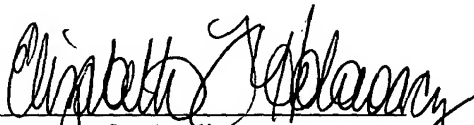
#### D. Remarks

The claims are 17-26, with claims 17 and 21 being independent. Claims 1-16 have been cancelled without prejudice or disclaimer. The pending claims correspond to non-elected and cancelled claims 23-32 from the parent application (09/695,925). Consideration of the present claims is respectfully requested.

The specification has been amended to make specific reference to the parent application, to more closely conform with proper idiomatic English, to correct minor typographical errors and to make changes similar to those made in the parent case. To this end, a substitute specification has been prepared. A copy of the marked-up original specification, indicating the changes that have been made, is enclosed. No new matter has been added to the present application in the preparation of the substitute specification.

Applicant's undersigned attorney may be reached in our New York office by telephone at (212) 218-2100. All correspondence should continue to be directed to our below listed address.

Respectfully submitted,

  
\_\_\_\_\_  
Attorney for Applicant  
Registration No. 42,667

FITZPATRICK, CELLA, HARPER & SCINTO  
30 Rockefeller Plaza  
New York, New York 10112-3801  
Facsimile: (212) 218-2200

NY\_MAIN 364890v1

This application is a division of application No. 09/695,925, filed October 26, 2000, which in turn is a division of application No. 08/743,375, filed November 4, 1996 (now U.S. Patent No. 6,217,665), which in turn is a continuation of application No. 08/013,314, filed February 4, 1993 (now abandoned).

APPARATUS FOR WASHING GLASS SUBSTRATES AND  
PROCESS FOR PRODUCING A LIQUID CRYSTAL DEVICE  
~~METHOD OF CLEANING SUBSTRATE~~

→ BACKGROUND

~~FIELD OF THE INVENTION AND RELATED ART~~ ←

The present invention relates to a method of  
5 cleaning substrates, particularly a method of cleaning  
substrates suitable for cleaning glass substrates for  
liquid crystal devices wherein dirt on a glass  
substrate causing an inferior product is removed  
during a liquid crystal device production process.

10 There have been known wet-cleaning techniques  
using pure water for cleaning substrates for precision  
devices or appliances, such as glass substrates for  
liquid crystal devices. In the case of cleaning a  
glass substrate for a liquid crystal device already  
15 provided with a pattern of electrodes and before  
provision of an alignment film, for example, it has  
been ordinarily practiced to first remove dirt, such  
as dust and inorganic matter, by a combination of  
spraying, high-pressure showering and/or ultrasonic  
20 cleaning respectively using pure water, optionally  
with brushing or ultrasonic cleaning with a detergent  
and cationic pure water as a pretreatment, and drain  
the water as by an air knife, a spinner or pulling out  
from warm pure water, or dry the substrate with, e.g.,  
25 vapor of IPA (isopropyl alcohol).

It is also known to thereafter heat the glass  
substrate to about 150 °C and irradiate the substrate

with ultraviolet rays at wavelengths of 184.9 nm and 253.7 nm so as to have oxygen in <sup>the</sup> air absorb the ultraviolet rays at 184.9 nm to generate ozone and have the ozone absorb the ultraviolet rays at 253.7 nm to generate oxygen radicals, by which organic matter is decomposed and removed.

However, the above-mentioned first washing with pure water for removal of dust or inorganic matter with pure water as by a combination of spraying, high-pressure showering, ultrasonic cleaning, etc., requires some length of time, thus leading to an inferior throughput of the cleaning apparatus or requiring an elongated apparatus in order to retain a high throughput ~~by~~ using the same length of time. Further, a large amount of water is required per sheet of glass substrate, and the cleaning cost is considerably expensive.

Further, if the pre-cleaning by brushing or ultrasonic cleaning using a detergent is performed before the cleaning with pure water, it is possible to obtain a sufficient cleaning effect even if a shorter time is used for the cleaning with pure water. However, for an identical throughput, this additionally requires a cleaning step using a detergent and a <sup>n</sup> rising step, so that the total length of the required cleaning apparatus is not substantially changed. Further, the required amount

of pure water is not substantially charged<sup>n</sup> either because the rinsing step after the cleaning with a detergent requires an additional amount of pure water, thus also requiring a high process cost.

5

→ SUMMARY OF THE INVENTION ←

In order to solve the above-mentioned problems, an object of the present invention is to provide a method of cleaning a substrate, whereby  
10 dirt, such as inorganic and organic matters, can be effectively removed while shortening the wet cleaning time and reducing the amount of water used.

Another object of the present invention is to provide a method of cleaning a substrate, whereby a  
15 glass substrate can be effectively cleaned with a minimum amount of pure water and a short time with a simple apparatus arrangement and without complex process control.

According to the present invention, there is  
20 provided a method of cleaning a substrate for removing dirt on the substrate, comprising<sup>✓</sup> irradiating a substrate surface with ultraviolet rays including wavelengths of 184.9 nm and 253.7 nm in an oxygen-containing atmosphere, and then subjecting the  
25 substrate to wet cleaning with pure water.

These and other objects, features and advantages of the present invention will become more

apparent upon a consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawings.

5

→ BRIEF DESCRIPTION OF THE DRAWINGS ←

Figure 1 is an illustration of a batch-type cleaning apparatus for use in a method of cleaning a substrate according to the present invention.

10

Figure 2 is an illustration of a sheet-by-sheet type cleaning apparatus for use in a method of cleaning a substrate according to the present invention.

→ 15 DESCRIPTION OF THE PREFERRED EMBODIMENTS ←

In a preferred embodiment of the present invention, a glass substrate for a liquid crystal device may be cleaned for removal of dirt thereon by first irradiating a surface of the substrate with  
20 ultraviolet rays including wavelengths of 184.9 nm and 253.7 nm in an oxygen-containing atmosphere and then subjecting the substrate to wet cleaning with pure water.

More specifically, in the cleaning method for  
25 removing dirt (foreign matter) on a glass substrate according to the present invention, immediately before the wet cleaning with pure water of the substrate, the

surface of the substrate is simultaneously irradiated with ultraviolet rays including components with wavelengths of 184.9 nm and 253.7 nm, preferably having peaks at these wavelengths, whereby oxygen in the atmosphere absorbs ultraviolet rays at 184.9 nm to form ozone and the ozone absorbs ultraviolet rays at 253.7 nm to form oxygen radicals, with which the dirt of organic matter on the glass substrate is chemically removed and the surface tension of the glass surface is reduced to improve the wettability in advance to enhance the effect of cleaning dirt of inorganic matter in a subsequent cleaning step with pure water.

The irradiation means for issuing the above-mentioned wavelengths may be any, provided that they include sufficient amount of the above-mentioned wavelengths. Examples of which may include: discharge lamps, such as low-pressure mercury lamps, black-light fluorescent lamps, fluorescent chemical lamps, mercury arc lamps, and xenon arc lamps, and excimer lasers, such as KrF and ArF excimer lasers.

Such irradiation means can be combined in a plurality as desired. It is also possible to use separate irradiation means for a wavelength of 184.9 nm and a wavelength of 253.7 nm.

The irradiation intensity of the ultraviolet rays can be varied depending on the degree of soiling or dirt on the substrate or desired cleanliness of the

substrate but may generally preferably be at least 0.2 J/cm<sup>2</sup>, more preferably at least 0.4 J/cm<sup>2</sup>.

The irradiation of the substrate with ultraviolet <sup>radiation</sup> ~~ray~~ may be performed in an oxygen-

5 containing atmosphere, which may conveniently be atmospheric air or preferably be an oxygen atmosphere or an atmosphere containing oxygen diluted with an inert gas, such as Ar or N<sub>2</sub> so as to further obviate unnecessary by-products due to irradiation with  
10 ultraviolet rays.

The time after the ultraviolet irradiation until the cleaning with pure water may generally be at most 30 min<sup>utes</sup>, preferably at most 10 min<sup>utes</sup>. In other words, the cleaning with pure water may preferably be  
15 performed when the substrate surface shows a contact angle with water of at most 10 degrees, preferably at most 5 degrees. This means that the cleaning with pure water is started while the substrate surface shows good wettability with pure water.

20 Anyway, standing for a long time after the ultraviolet irradiation should be <sup>avoided</sup> ~~obviated~~ since the effect of the ultraviolet irradiation is lost.

Hereinbelow, the present invention will be described with reference to an embodiment shown in the  
25 drawings.

Example 1

Figure 1 is an illustration of an outline of



a batch-type cleaning apparatus for use in a method of cleaning substrates for, e.g., liquid crystal devices. Referring to Figure 1, the apparatus included an ultraviolet ray irradiation unit 1, wherein 7 U-shaped  
5 low pressure mercury lamps of 110 watts ("UVU-110", available from K.K. Oak Seisakusho) having two peaks and wavelengths of 184.9 nm and 253.7 nm were arranged. Into the unit 1, glass substrates 3 (300 mm x 300 mm x 1.1 mm-t), each provided with a surface  
10 pattern of electrodes and held in a cleaning cassette 4, were supplied sheet by sheet for irradiation with ultraviolet rays for 30 seconds per sheet from a distance of about 10 mm.

Then, by an automatic conveying machine 5, 5  
15 sheets of the glass substrates 3 subjected to the ultraviolet irradiation together with the cleaning cassette 4 were dipped and washed for about 180 seconds in a first ultrasonic cleaning vessel 5 using pure water, and then dipped and washed for about 180 seconds  
20 in a second ultrasonic cleaning bath 6, followed by drying with IPA (isopropyl alcohol) vapor in a chamber 7-1 in a drying vessel 7. The substrates thus cleaned were then taken out from the cleaning apparatus and subjected to coating with a polyimide forming liquid  
25 by flexographic printing, whereby a clear polyimide film was found to be formed thereon. The first and second cleaning vessels 5 and 6 were respectively

supplied with 500 liters/hour of pure water and, as a result of simple calculation, the substrates were sufficiently cleaned with pure water in a small amount of about 8 liters/sheet.

5           In contrast thereto, the same level of cleaning required about 16 liters/sheet without the preliminary ultraviolet irradiation prior to the cleaning with pure water.

          For evaluating the cleaning performance,  
10 glass substrates 3 were intentionally soiled with silica latex particles with an average particle size of 1.2  $\mu\text{m}$  at a rate of about 300 particles/ $\text{mm}^2$  and then cleaned in the above-described manner, whereby an extremely good removal rate of 98 % was obtained.

15           In contrast thereto, when substrates intentionally soiled similarly as above were cleaned without being introduced into the ultraviolet ray irradiation unit 1, i.e., by directly introduced into the first cleaning bath 5, the second cleaning bath 6  
20 and the drying bath 7, a removal rate of only 92 % was obtained showing a clearly inferior cleaning state than in the case where the ultraviolet irradiation was performed in advance of the cleaning with pure water. Further, in order to obtain a removal rate of 98 %, it  
25 was necessary to effect the cleaning sequence though the vessels 5 - 7 two cycles under identical conditions.

Example 2

Figure 2 is an illustration of a sheet-by-sheet cleaning apparatus for practicing a cleaning method for liquid crystal device substrates.

- 5 Referring to Figure 2, the apparatus included an ultraviolet ray irradiation unit 1 wherein 5 U-shaped 110 watt ~~low~~ <sup>g</sup> pressure mercury lamps ("UVU-110", available from K.K. Oak Seisakusho) having two peaks at wavelengths of 184.9 nm and ~~235.7~~ <sup>257.7</sup> nm were arranged.
- 10 Through the unit 1, glass substrates 3 (300 mm x 300 mm x 1.1 mm-t), each provided with a transparent electrode film (ITO) on the entirety of one face, were conveyed continuously sheet by sheet to be irradiated with ultraviolet rays from a height of 10 mm for about
- 15 40 seconds.

Then, the substrates 3 were subjected to wet cleaning by being sprayed with warm pure water at about 30 °C from a spray nozzle 9 and then subjected to high <sup>g</sup> pressure showering of pure water at about 15

20 kg.f/cm<sup>2</sup> from a shower nozzle 10, followed by draining with air knife 11. The thus cleaned substrates were then satisfactorily coated with a positive-type photoresist by roller coating, followed by satisfactory patterning of the ITO film.

- 25 For evaluating the cleaning performance similarly as in Example 1, substrates 3 were intentionally soiled with silica latex particles with

an average particle size of 1.2  $\mu\text{m}$  at a rate of about 300 particles/ $\text{mm}^2$  and then cleaned in the above-described manner, whereby a good removal rate of 96 % was obtained in the case where the ultraviolet

5 irradiation was performed before the cleaning with pure water. In contrast thereto, an inferior cleaning rate of about 89 % was measured in the case where the wet cleaning alone was performed.

Example 3

10 The substrates cleaned in Examples 1 and 2 were again subjected to irradiation with ultraviolet rays in an oxygen-containing atmosphere under similar conditions as in the <sup>previous</sup> ~~respective~~ <sup>a</sup> Examples, whereby further effective cleaning of the substrate surfaces  
15 could be performed.

As described hereinabove, according to the present invention, a substrate surface is irradiated with ultraviolet rays including wavelengths at 184.9 nm and 253.7 nm in an oxygen-containing atmosphere  
20 immediately before wet <sup>g</sup>cleaning with pure water, whereby it becomes possible to increase the removal rate of dirt, particularly of inorganic matter. As a result, it is possible to shorten the wet <sup>g</sup>cleaning time and decrease the amount of pure water, leading to  
25 a decrease in production cost.

→ ABSTRACT OF THE DISCLOSURE ←

Dirt, particularly of inorganic matter,  
attached to a substrate, such as a glass substrate for  
liquid crystal devices, is effectively removed by  
5 irradiating the substrate with ultraviolet rays  
including 184.9 nm and 253.7 nm in an oxygen-  
containing atmosphere in advance of wet cleaning with  
pure water. As a result, the wet cleaning time and  
the amount of pure water can be reduced.

10

15

20

25